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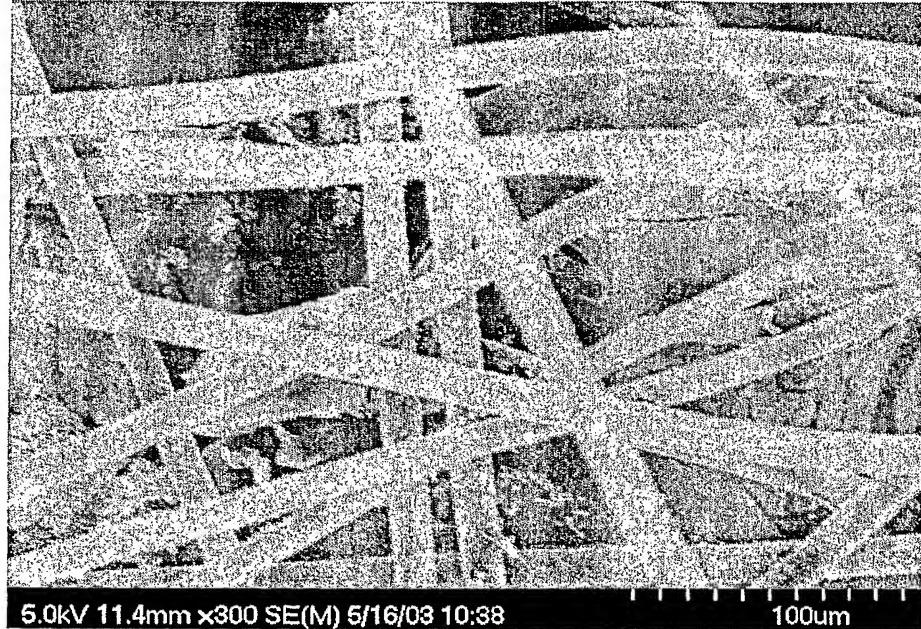
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(54) Title: HIGH SURFACE AREA CERAMIC COATED FIBERS



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(57) Abstract: A method of manufacturing a ceramic coated fiber comprises heat treating an activated carbon coated fiber containing a ceramic precursor in a liquid form, to form a ceramic coated fiber.



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HIGH SURFACE AREA CERAMIC COATED FIBERS

BACKGROUND

More than 700 organic compounds have been identified in sources of drinking water in the United States (Stachka and Pontius, 1984) and elsewhere.

Many water utilities, companies and government agencies must remove or destroy organic compounds from polluted groundwater supplies before those groundwater supplies can be used as drinking water. Additionally, many drinking water utilities are faced with the formation of disinfection by-products in finished water.

Disinfection by-products are compounds formed in the water treatment process as a result of the disinfection process. In this process, a disinfectant such as chlorine is added to source water, where it reacts with a portion of the background organic matter (BOM) present in the source water to produce disinfection by-products.

The reactive portions of the BOM are referred to as disinfection by-product precursors.

Considerable research is being directed at effective and economical treatment strategies that minimize the production of disinfection by-products. Advanced oxidation processes (AOPs) are alternative processes which destroy organic compounds and turn them into nontoxic forms, such as carbon dioxide and water. AOPs involve the generation of highly reactive radicals, such as the hydroxyl radical ($\text{OH}\cdot$), which are responsible for the destruction of the organic compounds. AOPs can be classified into two major groups: AOPs involving homogeneous reactions using hydrogen peroxide (H_2O_2), ozone (O_3), chlorine, and ultraviolet (UV) light, alone or in combination; and AOPs employing heterogeneous reactions using photoactive catalysts, such as semiconductors like titanium dioxide (TiO_2) and nitrogen-doped titanium dioxide ($\text{TiO}_{2-x}\text{N}_x$). In the latter case -- the photocatalytic oxidation processes -- photoactive semiconductor catalysts are immersed in an oxygenated aqueous solution and illuminated with UV or visible radiation, so that reactive oxygen species are produced, causing the oxidation of organic compounds.

-2-

The primary oxidant responsible for the photocatalytic oxidation of organic compounds in aqueous solutions is believed to be the highly reactive hydroxyl radical (OH^\cdot), although direct reactions of adsorbed organic compounds with surface species, such as holes, have also been reported (Völz et al., 1981; Ceresa et al., Matthews, 1984; and Turchi and Ollis, 1990). When a photoactive semiconductor is illuminated with photons of the band gap energy of the semiconductor, or greater, photons excite electrons from the valence band, overcoming the energy of the band gap to the conduction band, and leaves electron vacancies, or holes, in the valence band. For example, the anatase form of TiO_2 has a band-gap energy of about 3.2 eV, which is equivalent to the energy of UV light with a wavelength of 387 nm. Consequently, the anatase form of TiO_2 can be activated by radiation with wavelengths less than 387 nm. The excited electrons and the resulting holes may take part in redox processes with adsorbed species, such as H_2O , OH^\cdot , organic compounds and O_2 at the water-solid interface. The holes may take part in oxidation half reactions with adsorbed H_2O or OH^\cdot to form hydroxyl radicals. The electrons take part in the reduction half reactions with adsorbed O_2 to produce the superoxide radical O_2^\cdot , which may also in turn produce H_2O_2 and OH^\cdot (Okamoto et al., 1985).

For high photocatalytic efficiency, mesoporous TiO_2 with its large surface area is highly desirable, and it was first prepared using a phosphate surfactant through a modified sol-gel process. The product was not pure TiO_2 because of significant amounts of residual phosphorus, and its mesoporous structure underwent partial collapse during template removal by calcination. Another approach produced mesoporous TiO_2 from amphiphilic poly(alkylene) block copolymers as structure-directing agents and organic titanium salts as precursors in a non-aqueous solution. Slight changes in reaction conditions, however, often produced very different results, rendering this method difficult to reproduce. A third method, using dodecylamine as a directing agent and titanium isopropoxide as the precursor, and emptying the pores by extractions, yielded a porous structure that was not retained after heat treatment in dry air at 300 °C. Thus, it has so far

-3-

been difficult to produce the highly crystalline TiO₂ that is required for photocatalysis.

A second issue of current TiO₂ photocatalysis technology is the requirement of ultraviolet light for activation. Because of the large energy of the band gap of TiO₂ ($E_g = 3.2$ eV in anatase), its use as a photocatalyst is limited to radiation with a wavelength of less than 380 nm. A material catalytically active when exposed to visible light of wavelengths longer than 380 nm would allow for satisfactory photocatalysis in environments where less intense light is available, for instance indoors or in a vehicle.

A further major issue of the current technology is that the powder form of the photocatalyst is difficult to handle, and too fine to be recovered from photoreactors. Thus, several films of TiO₂ on various substrates and supports have been developed for photocatalytic applications. However, particle sintering and agglomeration greatly reduce the surface area of the photocatalyst.

The bonding of the TiO₂ to the substrate is also a source of problems. Films of TiO₂ have been assembled on substrates by direct growth and post synthetic crystal attachment. Both methods rely on chemical binders to immobilize TiO₂ to the substrate surface. Unfortunately, organic binders are susceptible to decomposition under UV light. Consequently, the TiO₂ films become loose from the substrate, and are easily detached.

Powders, fibers and films of TiO₂ have been reported, and a number of photocatalytic TiO₂ powder preparations are commercially available. However, these powders are difficult to apply to water purification, and the surface area of the powders is low, resulting in low catalytic activity and only a small number of catalytic sites.

In contrast, TiO₂ fibers have a very high surface area, high wear and mechanical strength, and high thermal stability. Moreover, when used in chemical reactors, TiO₂ fibers cause only a small pressure drop and can serve as a reinforcement material and as a matrix of various shapes and sizes.

TiO₂ fibers may be prepared by various fabrication methods. For example, TiO₂ fibers were prepared by solvothermal reaction of a fibrous K₂Ti₄O₉

-4-

precursor, by ion-exchange reaction of $K_2O \cdot 4TiO_2$ fibers and thermal decomposition of $H_2Ti_4O_9$.

Activated carbon fibers (ACF) are traditionally produced by heating an organic precursor until carbonized, and then activating the carbonized material. Activation is achieved typically by heating the carbonized material in an oxidizing environment. Alternatively, the carbon may be activated chemically. This process involves impregnating the carbon precursor with, for example, phosphoric acid, zinc chloride, or potassium hydroxide, followed by carbonization.

The above methods, however, yields brittle and frangible ACF, limiting their use to systems containing some mechanical support. This problem has been mitigated by preparing fibers where activated carbon is formed as a coating on substrate fibers.

For example, U.S. Patent No. 5,834,114 describes glass or mineral fibers coated with activated carbon. These are prepared by coating the fiber substrate with a resin, cross-linking the resin, heating the coated fiber substrate and resin to carbonize the resin, and exposing the coated fiber substrate to an etchant to activate the coated fiber substrate.

U.S. Patent No. 6,517, 906 describes coating the substrate fibers with a mixture containing an organic polymeric material, and a chemical activating agent, for example a Lewis acid or base. This mixture carbonizes at temperatures lower than those required by earlier methods, allowing for the formation of activated carbon coatings on low melting point fibers, such as HEPA fibers.

SUMMARY

In a first aspect, the present invention is a method of manufacturing a ceramic coated fiber, comprising heat treating an activated carbon coated fiber containing a ceramic precursor, to form a ceramic coated fiber.

In a second aspect, the present invention is a ceramic coated fiber, comprising (a) a fiber, and (b) ceramic, coated on the fiber. The ceramic has a BET surface area of at least 60 m²/g, and the ceramic comprises crystalline ceramic.

In a third aspect, the present invention is a method for manufacturing an intermediate for the fabrication of ceramic coated fibers, comprising heating an activated carbon coated fiber containing a ceramic precursor, to cure the precursor.

5 In a fourth aspect, the present invention is a ceramic coated fiber comprising (a) a fiber, and (b) ceramic, coated on the fiber. The ceramic has a BET surface area of at least 50 m²/g, and the ceramic comprises at least one member selected from the group consisting of Al₂O₃, ZrO₂, and MgO.

BRIEF DESCRIPTION OF THE FIGURES

10 Figure 1 illustrates a surface electron micrograph (SEM) of ceramic fibers produced according to the method of Example 1.

Figure 2 illustrates the photodegradation of stearic acid catalyzed by the fibers of Example 1 (Figure 2A), and by a reference commercial TiO₂ photocatalyst (Figure 2B).

15 Figure 3 illustrates the photodegradation of stearic acid catalyzed by the fibers of Example 1 (Figure 3A), and by a reference commercial TiO₂ photocatalyst (Figure 3B).

Figure 4 illustrates the photodegradation of humic acid catalyzed by the TiON fibers of Example (3).

20 Figure 5 illustrates the incubation of an *E. coli* bacterial culture with the TiON fibers of Example (3) and with the Ag-TiON fibers of Example (5).

Figure 6 illustrates the effect of ACF on surface areas and yield of Al₂O₃ fibers.

25 Figure 7 illustrates the effect of the temperature of the second heating on the surface areas and the yield of Al₂O₃ fibers.

Figure 8 illustrates the effect of the temperature of the second heating on the surface area and the yield of MgO fibers.

DETAILED DESCRIPTION

Activated carbon does not resist temperatures higher than 573 K in an oxidative atmosphere. Therefore, it had been thought to be inapplicable to use activated carbon as a substrate fiber for fabrication processes requiring high temperature calcination, such as the manufacturing of ceramic coated fibers. The present invention is based on the discovery that, despite this instability at high temperatures, activated carbon can be used as a template in the formation of ceramic coated fibers.

Activated carbon coated fibers are first prepared by coating substrate fibers with activated carbon or an activated organic coating as described in U.S. Patent No. 6,517, 906. Example substrate fibers include HEPA filters, synthetic fibers used in clothing, polyesters, polyethylene, polyethylene terephthalate, nylon 6, nylon 66, polypropylene, KEVLARTM, TEFLONTM, liquid crystalline polyesters, and syndiotactic polystyrene. Glass fibers such as e-glass fibers; mineral fibers such as asbestos and basalt; ceramic fibers such as TiO₂, SiC, and BN; metal fibers (or wires) such as iron, nickel, gold, silver, aluminum and platinum; polymer fibers such as TYVEKTM; and combinations thereof. Some preferred substrate fibers are listed in the table below.

Company	Product Line	Description
CRANE & CO.	Crane 230 (6.5μm) Crane 232 (7.5μm)	Non-woven Fiber Glass Mats Non-woven Fiber Glass Mats
FIBRE GLAST	519 (0.75 oz.) 573 (9 oz.)	wovens wovens
HOLLINGSWORT H & VOSE	BG05095 HE1021	glass paper or felts
JOHNS MANVILLE	7529 (11μm)	non-woven fiber glass mats
LYDALL MANNING	MANNIGLAS®	non-woven fiber glass mats
DUPONT	TYVEK®	HDPE Spun bonded paper

The substrate fibers may be present in any form. Examples include loose fibers, woven and non-woven fabrics, papers, felts and mats. The substrate fibers may be made from substrate fibers already present in a specific form, or the substrate fibers may first be prepared from loose substrate fibers, and made into the specific form. The length of the substrate fibers is not limited, and may be, for example, 0.01 mm to over 100 m in length, but preferably at least 3 micrometers. The substrate fibers may be prepared from longer substrate fibers, then cut or chopped. Furthermore, the diameter of the substrate fibers is also not limited, and may be, for example 100 Å to 1 mm in diameter. Preferably, the fibers have an aspect ratio of at least 10.

If the substrate fibers are susceptible to oxidation, it may be advantageous to coat them with an oxidation resistant coating, before forming the activated carbon on the fibers. Examples of oxidation resistant coating include water glass and phosphate glass.

The activated carbon coated fibers are infiltrated with ceramic precursors by immersion in a solution of one or more ceramic precursors in a volatile solvent. In general, ceramic precursors are compounds of one or more elements present in the ceramic and volatile components, such as halides, nitrates, nitrides, nitrates, hydroxides, organic acid salts and organometallic complexes. When subjected to high temperature treatment, the ceramic elements and any oxygen are left as a ceramic deposit, whereas the remainder of the precursor is volatilized.

Ceramic precursors are soluble compounds of the first group, second group, third group, fourth group, the transition metals, the lanthanide and actinide elements, N, O, Se, Te, and Po. Example ceramic precursors include $Ti(t\text{-}BuO)_4$, $Ti(i\text{-}Pr)_4$, $Si(OEt)_4$, $ZnCl_2$, $ZrOCl_2$, $ZrO(OH)Cl$, $Zr(COOCH_3)_4$, $MgCl_2$, $Mg(COOCH_3)_2$, and $MgSO_4$. A mixture of two or more precursors may be used, for instance if a secondary, ternary or quaternary ceramic compound is desired. An oxynitride ceramic coating may be obtained by adding a nitrogen dopant such as a tetraalkylammonium salt. Likewise, an oxysulfide coating may be made by adding a sulfur dopant such as thiourea.

The excess precursor is removed, and the infiltrated precursor may be hydrolyzed by exposure to the moisture in the air, yielding a composite of carbon and the precursor or the hydrolyzed precursor.

The ceramic precursor should preferably accumulate in the pores of the template to form an interconnected solid or gel. The system is then subjected to a heat treatment, which may remove residual solvent, cure the precursor, as well as remove the activated carbon, and crystallize the ceramic. For example, the heat treatment may include a first heating at 250 °C to 600 °C, or 250 °C to 400 °C, optionally in an inert atmosphere, to remove residual solvents and to cure the ceramic precursor. A second heating may follow, for example at 400 °C to 1000 °C, in an oxidizing atmosphere, removing the carbon substrate and crystallizing the ceramic, and if necessary, oxidizing the cured precursor. The carbon substrate may also be oxidized by irradiation of the fibers, or by treatment with chemical oxidizers.

The resulting fibers may be further modified by adding one or more additional precursors, for example AgNO₃ or Pd(acac)₂, followed by additional rounds of heating. Such heating may be carried out in a reducing atmosphere, such as an atmosphere containing H₂.

For example, activated carbon coated fibers may be used to prepare Al₂O₃ coated fibers. To this end, ACF may be impregnated in an aqueous solution of AlCl₃, dried, and heat-treated under N₂ at a temperature of usually 500 °C to 700 °C. A second heat treatment, this time in an oxidizing atmosphere, removes the carbon. The material is then calcined, yielding thermally stable Al₂O₃ coated fibers.

When the temperature of the second heat treatment is about 500 °C or above, air is preferred as an oxidizing atmosphere, as opposed to pure O₂. For lower temperatures, such as 450 °C, pure O₂ is preferable. In general, lower temperatures require longer heating times for the complete removal of the carbon template. For instance, at 500 °C, it usually takes more than 24 hours to burn off the template, whereas only a few seconds of heating are needed at 900 °C. Lower temperatures also yields Al₂O₃ coated fibers with a higher Brunauer-Emmett-

-9-

Teller (BET) surface area and a poorly crystalline structure. By contrast, higher temperature yields fibers with a lower BET surface area and the ceramic is more crystalline.

The ceramic coating may be present on isolated regions on the surface of the substrate fibers, may completely enclose the substrate fibers, or enclose all of the substrate fibers except the ends of the substrate fibers. For example, if the substrate fibers were completely enclosed by the ceramic coating, then chopping would result in the ends of the fibers being exposed.

The weight ratio between the ceramic coating and the substrate fibers in the ceramic coated product fibers is not limited, but does affect final properties. For example, if the amount of the ceramic coating is very large compared to the amount of substrate fibers, then the brittleness of the ceramic coating may reduce the flexibility of the product ceramic coated fibers. Preferably, the product ceramic coated fibers include 10 to 90% by weight of the nanoporous organosilica ceramic coating, more preferably 20 to 80% by weight of the ceramic coating, including 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, and 90% by weight of the ceramic coating.

Ceramic coated fibers may have BET surface areas of at least 50 m²/g, preferably more than 50 m²/g, more preferably at least 60 m²/g, including 60-2000 m²/g, and 100-500m²/g. Preferably, the ceramic of the ceramic coated fibers contains crystalline ceramic, and may also include an amorphous phase. The crystallites (or particles) of ceramic preferably have an average particle diameter of 2 nm to 50 nm. Even though the temperatures used to form the ceramic coated fibers may appear insufficient for crystallization of the bulk ceramic, crystalline material is present. One possible explanation is that the activated carbon catalyzes the crystallization of the ceramic. Furthermore, the coating holds to the fiber without the need for any binders.

The ceramic coated fibers of the invention may be used to catalyze photochemical reactions, for example for the photodegradation of unwanted organic and biological compounds or the disinfection of bacteria. Thus, the fibers may be used for the purification and sterilization of water and air, or for the disinfection of tools such as medical room utensils. Other uses include substrates

-10-

for catalytic material (for example, platinum), and abrasive materials. The fibers of the invention may also be manufactured with conductive fibers, such as metal fibers. Thus, product fibers with a metal core and a catalytic oxide surface may be formed, and use as sensors, for instance as oxygen sensors to monitor combustion.

5 EXAMPLES

(1) TiO_2 fibers

A carbon template was prepared by coating glass fibers with PAN resin prior to activation. After activation with H_2O , the surface area of carbon was 1800 m²/g and the pore size was from 1 nm to 10 nm. The pore system of the carbon template was then infiltrated with titanium tetraisopropoxide (TTIP) by wet impregnation for 24 hours at room temperature (20-22 °C). After removing the TTIP by washing with ethanol, precursor hydrolysis was initiated by exposure to air moisture. Mesoporous inorganic particles were then obtained by crystallization or polymerization of TiO_2 at 250 - 400 °C in a nitrogen atmosphere for 4 hours, followed by removal of the carbon in air at the heating rate of 1 C/min. The surface area of the final product fibers was 500 m²/g, based on the TiO_2 weight.

Figure 1 illustrates a surface electron micrograph (SEM) of the product fibers.

(2) TiO_2 fibers

An activated carbon coated fiber was made by coating glass fiber with phenolic resin prior to activation. Following activation with N_2 , the surface area of the carbon was about 1200m²/g, and the pore size was from 1 to 3 nm. The pore system of the activated carbon coated fiber was infiltrated with the titanium n-butoxide by wet impregnation for 24 h at room temperature. After removal of excess n-butoxide by ethanol wash, the hydrolysis of precursor was initiated by exposure to air moisture. Mesoporous inorganic particles, with an average particle diameter from about 2 nm to about 50 nm, were then obtained by crystallization or polymerization of TiO_2 at 300 °C in air for 4 hours, followed by removal of the

-11-

carbon at 550 °C in air for 2 hours. The surface area was 230 m²/g based on the TiO₂ weight.

(3) TiON fibers

The activated carbon coated fiber was made by coating glass fibers with PAN resin prior to activation. After activation with H₂O, the surface area of the carbon was about 1800m²/g, and the pore size was about 1 nm. The pore system of activated carbon coated fiber was infiltrated with a 100:2 mixture of titanium tetroisopropoxide and a nitrogen dopant tetramethylammonium salt by wet impregnation for 24 h at room temperature. The surface was washed with ethanol, and the hydrolysis of the precursor was initiated by exposure to air moisture. The mesoporous inorganic spheres were then obtained by crystallization or polymerization of the TiON at 300 °C in air for 1 h, followed by removal of the carbon and of the nitrogen dopant at 500 °C in air for 3 h.

(4) TiOS fibers

Two grams of thiourea were dissolved in 20 g of N, N-dimethylformamide (DMF) and added to 10g TTIP, and 2 g of ethanol were added to the mixture to obtain a transparent solution. The activated carbon coated fiber was made by coating glass fiber with PAN or phenolic resin prior to activation. After activation with H₂O, the surface area of carbon was about 1800m²/g and the pore size was about 1 nm. The pore system of the activated carbon coated fiber was infiltrated with the above-described solution by wet impregnation for 24 hours at room temperature. The carbon surface was washed with acetone, and the hydrolysis of the precursor was initiated by exposure to air moisture. The mesoporous inorganic spheres were then obtained by crystallization or polymerization of TiOS at 500 °C in air for 3 hours, followed by removal of the carbon and of the sulfur dopant at 500 °C in air for 1 hours.

-12-

(5) Ag-TiON fibers

TiON fibers prepared according to the method of Example (3) were immersed in a 10% (wt) silver nitrate solution for 12 hours at room temperature. The fibers were then washed with de-ionized (DI) water and heated at 300 °C for 2 hours.

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(6) Pd-TiON fibers

TiON fibers prepared according to the method of Example (3) were immersed in a 1% (wt) $\text{Pd}(\text{acac})_2$ toluene solution for 12 hours at room 10 temperature. The fibers were then heated at 400 °C for 1 hour and reduced in H_2 at 200 °C for 3 hours.

(7) Photodegradation with TiO_2 fibers and 254 nm light

The photodegradation rate of stearic acid is commonly used to assay the 15 photocatalytic activity of semiconductor films. Accordingly, stearic acid was deposited on a 10 mm x 10 mm fiber sample by dip coating the fiber in a methanolic solution of stearic acid 0.02 M. The photocatalytic activity was compared to that of a reference photocatalyst film obtained by deposition of 20 commercial TiO_2 (Hombikat UV 100) slurry via dip coating followed by washing in distilled water and drying in air for 1 hour at 80 °C. The degradation rates of stearic acid were calculated by measuring the integrated absorbance of stearic acid between 2700 and 3000 cm^{-1} in the infrared spectrum. After a 2 hours-long 25 exposure to a light source of 254 nm wavelength and 2.8 mW/cm^2 intensity, the percentage of degraded stearic acid was 39% for the mesoporous TiO_2 fibers of the invention, as illustrated in Figure 2A, and 27% for the reference photocatalyst, as illustrated in Figure 2B..

(8) Photodegradation with TiO_2 fibers and 365 nm light

The procedure of Example (7) was followed, with a 12 hours-long 30 exposure to a light source of 365 nm wavelength and 2.4 mW/cm^2 intensity. The percentage of degraded stearic acid was 73% for the mesoporous TiO_2 fibers of the

-13-

invention, as illustrated in Figure 3A, and 42% for the reference photocatalyst, as illustrated in Figure 3B.

(9) Photodegradation of humic acid with TiON fibers

5 Humic acid was deposited on a 10 mm x 10 mm sample of the TiON fibers of Example (3) by dip coating in a 0.25%(wt) aqueous humic acid solution. A degradation experiment according to the procedure of Example (7) was then conducted under a visible light source with an intensity of 1.9 mW/cm². The degradation of the humic acid was calculated by monitoring the absorption 10 intensity of the humic acid solution at 400 nm in a UV-Vis spectrophotometer. As illustrated in Figure 4, after 8 hours of exposure to the light source, the TiON fiber of the invention had degraded 43% of the humic acid, whereas the reference photocatalyst of Example (7) showed no photocatalytic activity whatsoever.

15 (10) Disinfection of bacterial cultures

A culture of E. coli bacteria was grown aerobically in a test-tube at 37 °C for 18 hours. The TiON fibers of Example (3) and the Ag-TiON fibers of Example (5) were then tested as disinfectants on this culture by incubation under visible light at room temperature for 5 hours. Following the incubation, the 20 number of viable cells in the disinfected samples and in control samples was determined by serial dilutions followed by incubation at 37 °C for 24 hours. As illustrated in Figure 5, The TiON fiber destroyed more than 80% of the bacteria, whereas Ag-TiON destroyed all of the bacteria.

25 (11) Al₂O₃ fibers.

Commercially available activated carbon coated fiber manufactured by Nippon Kynol (Kansai, Japan), with various surface areas, were used as templates. The activated carbon coated fibers used for this example were designated ACF7, ACF10, ACF15, ACF20 and ACF25, with BET surface areas of 690, 738, 1390, 30 1590 and 1960 m²/g, respectively.

-14-

Activated carbon coated fiber was impregnated with an aqueous solution of AlCl₃, heat-dried at about 150 °C, then heat-treated under N₂ at a temperature of about 600 °C. A second heat treatment at 600 °C in air was then applied to remove the carbon template, and calcination of the product yielded thermally stable, 5 white-colored Al₂O₃ fibers. The removal of the carbon template was confirmed by thermal gravimetric analysis (TGA).

The N₂ absorption isotherms, the BET surface area and the pore size distribution of the product Al₂O₃ fibers were measured with an Autosor-1 (Quantachrome Corp., Boynton Beach, FL) volumetric sorption analyzer. As 10 illustrated in Figure 6, it appears that the BET surface area and the yield of Al₂O₃ fiber was directly proportional to the porosity of the ACF template. N₂ absorption isotherms at 77 K showed that the Al₂O₃ fibers were mesoporous materials, and pore distribution analysis showed peak values of mesopore in the range between 3.5 nm and 3.8 nm.

(12) Effect of template-removal temperature on product Al₂O₃ fibers
ACF23 (surface area = 1730 m²/g) was impregnated with an aqueous solution of AlCl₃, heat-dried at about 150 °C, then heat-treated under N₂ at a 20 temperature of about 600 °C. A second heat-treatment in air, at a temperature chosen from the range between 450 °C to 900 °C, was applied to remove the carbon template. A thermally stable, white-colored Al₂O₃ fiber was then obtained upon calcination. The removal of the carbon template was confirmed by thermal gravimetric analysis (TGA), and the crystalline phases present in the fibers were identified by powder X-ray diffraction on a Rigaku/D/max-VA (Rigaku/MSC, The 25 Woodlands, TX).

Illustrated in Figure 2 (7) are the effects of the carbon oxidation temperature on the surface area of the product fibers. At lower temperatures, for example 500 °C, the complete removal of the template required usually more than 24 hours. At higher temperatures, for example 900 °C, the template was 30 completely removed within seconds. The BET surface area of the Al₂O₃ fibers was higher for lower template-removal temperatures, and when the temperature was

-15-

500 °C and above, heating in air yielded better results than in O₂. However, when the temperature was as low as 450 °C, only O₂ could be used to remove all the carbon template, yielding a product with a very high BET surface area of above 500 m²/g.

5 N₂ absorption isotherms showed that Al₂O₃ fibers obtained at different template-removal temperatures were all mesoporous materials. X-ray diffractometry revealed an amorphous structure for fibers obtained at a template removal temperature of 450 °C, and more crystalline structures for higher template removal temperatures.

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(13) MgO fibers

15 ACF23 (surface area = 1730 m²/g) was impregnated in an aqueous solution of Mg(Ac)₂ obtained by dissolving 1 g of Mg(Ac)₂ in 2 mL of H₂O, heat-dried at about 150 °C, and then heat-treated in N₂ at about 600 °C. A second heat-treatment in air, at a temperature chosen from the range between 450 °C to 900 °C, was applied to remove the carbon. Calcination of the product yielded thermally stable, white-colored MgO fibers. The N₂ absorption isotherms, the BET surface area and the pore size distribution of the product Al₂O₃ fibers were measured with an Autosor-1 (Quantachrome Corp., Boynton Beach, FL) volumetric sorption analyzer. The removal of the carbon was confirmed by thermal gravimetric analysis (TGA), and the crystalline phases present in the fibers were identified by powder X-ray diffraction on a Rigaku D/max-VA (Rigaku/MSC, The Woodlands, TX).

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25 Illustrated in Figure 3 (8) are the effects of the carbon removal temperature on the surface area and the yield of the MgO fiber products. At lower carbon removal temperatures, such as 400 °C, longer periods of time were required to remove the carbon, and surface areas up to 250 m²/g were obtained. Higher carbon removal temperatures yielded fibers with lower surface areas. N₂ absorption isotherms showed that all the product MgO fibers were mesoporous materials. X-ray diffractometry of the fibers revealed a cubic MgO crystal structure.

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-16-

(14) ZrO₂ fibers

Two samples of ACF23 (surface area = 1730 m²/g) were impregnated with a Zr(NO₃)₄ aqueous solution obtained by dissolving 1 g of Zr(NO₃)₄ in 5 mL of water, heat-dried at about 150 °C, and then heat-treated in N₂ at about 600 °C. The first sample was then heat-treated in air at 450 °C, and the second sample was heat-treated in air at 600 °C. The fibers were then calcinated, yielding thermally stable, white-colored ZrO₂ fibers.

The N₂ absorption isotherms, the BET surface area and the pore size distribution of the product ZrO₂ fibers were measured with an Autosor-1 (Quantachrome Corp., Boynton Beach, FL) volumetric sorption analyzer. The fibers obtained from the first sample has a BET surface area of 50 m²/g, and the fibers obtained from the second sample had a BET surface area of 60 m²/g. X-ray diffractometry of the fibers revealed a tetragonal ZrO₂ crystalline structure.

CLAIMS

1. A method of manufacturing a ceramic coated fiber, comprising:
heat treating an activated carbon coated fiber containing a ceramic precursor, to form a ceramic coated fiber.
2. The method of claim 1, wherein the heat treating comprises:
a first heating at a temperature of at least 250 °C, to cure the precursor, and
a second heating, in an oxidizing atmosphere, at a temperature of at least 400 °C, to remove the carbon.
3. The method of any one of the preceding claims, wherein the first heating is in an inert atmosphere.
4. The method of any one of the preceding claims, wherein the ceramic comprises TiO₂ and/or TiON having an anatase structure.
5. The method of any one of the preceding claims, wherein the ceramic precursor further comprises a nitrogen or sulfur dopant.
6. The method of any one of the preceding claims, wherein the nitrogen source is tetramethylammonium hydroxide.
7. The method of any one of the preceding claims, further comprising:
contacting the ceramic coated fiber with a compound containing silver; and
a third heating of the ceramic coated fiber.
8. The method of any one of the preceding claims, further comprising:
contacting the ceramic coated fiber with a compound containing palladium;
a third heating of the ceramic coated fiber; and
a fourth heating of the ceramic coated fiber in an atmosphere comprising H₂.

9. The method of any one of the preceding claims, wherein the ceramic comprises crystalline ceramic and has a BET surface area of at least 50 m²/g.

10. The method of any one of the preceding claims, wherein the ceramic comprises at least one member selected from the group consisting of TiO₂, TiON, TiOS, Al₂O₃, ZrO₂, and MgO.

11. A ceramic coated fiber manufactured according to the method of any one of the preceding claims.

12. A method for producing radical species, comprising illuminating the fiber of claim 11,

wherein the ceramic comprises TiO₂ and/or TiON having an anatase structure.

13. A method for purifying and disinfecting air or water, comprising contacting the air or water with the fiber of claim 11 and illuminating the fiber,

wherein the ceramic comprises TiO₂ and/or TiON having an anatase structure.

14. A photochemical reactor comprising the fiber of claim 11,

wherein the ceramic comprises TiO₂ and/or TiON having an anatase structure.

15. A ceramic coated fiber, comprising:

(a) a fiber, and

(b) ceramic, coated on the fiber,

wherein the ceramic has a BET surface area of at least 60 m²/g, and the ceramic comprises crystalline ceramic.

16. The ceramic coated fiber of claim 15, wherein the ceramic comprises TiO₂ and/or TiON having an anatase structure.

17. The ceramic coated fiber of claim 15 or 16, wherein the ceramic comprises at least one member selected from the group consisting of TiO₂, TiON, TiOS, Al₂O₃, ZrO₂, and MgO.

18. The ceramic coated fiber of any one of claims 15 through 17, wherein the ceramic has a B.E.T. surface area of 60 m²/g to 300 m²/g.
19. The ceramic coated fiber of any one of claims 15 through 18, wherein the ceramic comprises 10 to 90% by weight of the ceramic coated fibers.
20. The ceramic coated fiber of any one of claims 15 through 19, further comprising silver and/or palladium.
21. A method for producing radical species, comprising illuminating the fiber of any one of claims 15 through 20.
22. A method for purifying and disinfecting air or water, comprising contacting the air or water with the fiber of any one of claims 15 through 20, and illuminating the fiber.
23. A photochemical reactor comprising the fiber of any one of claims 15 through 20.
24. A method for manufacturing an intermediate for the fabrication of ceramic coated fibers, comprising heating an activated carbon coated fiber containing a ceramic precursor, to cure the precursor.
25. The method of claim 24, wherein the heating is in an inert atmosphere.
26. An intermediate for the fabrication of ceramic coated fibers manufactured according to the method of claim 24 or 25.
27. A ceramic coated fiber, comprising:
 - (a) a fiber, and
 - (b) ceramic, coated on the fiber,wherein the ceramic has a BET surface area of at least 50 m²/g, and the ceramic comprises at least one member selected from the group consisting of Al₂O₃, ZrO₂, and MgO.

28. The ceramic coated fiber of claim 27, wherein the ceramic has a B.E.T. surface area of 60 m²/g to 300 m²/g.
29. The ceramic coated fiber of claim 27 or 28, wherein the ceramic comprises 10 to 90% by weight of the ceramic coated fibers.
30. The ceramic coated fiber of claim 27 through 29, further comprising silver and/or palladium.

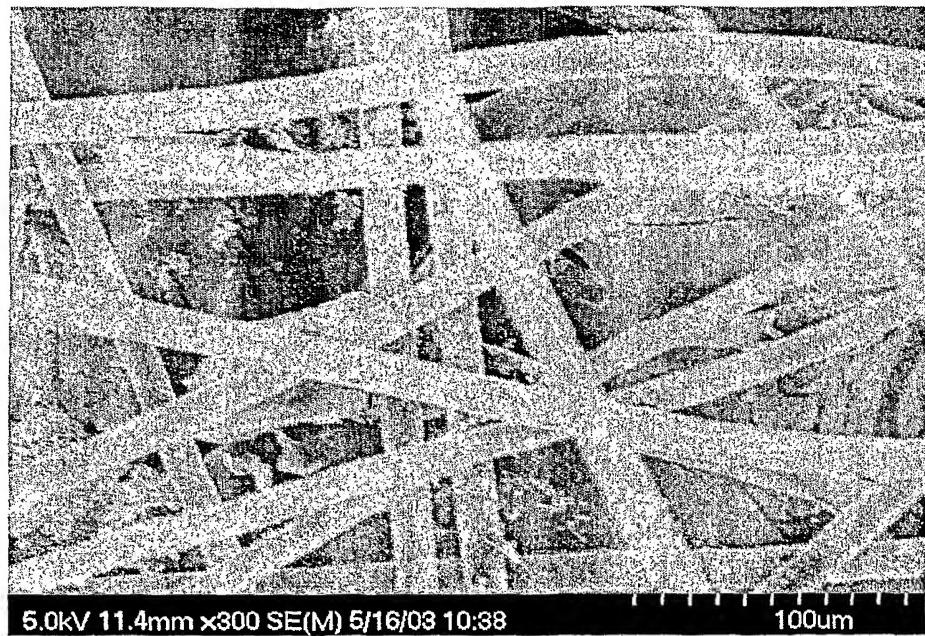


Figure 1

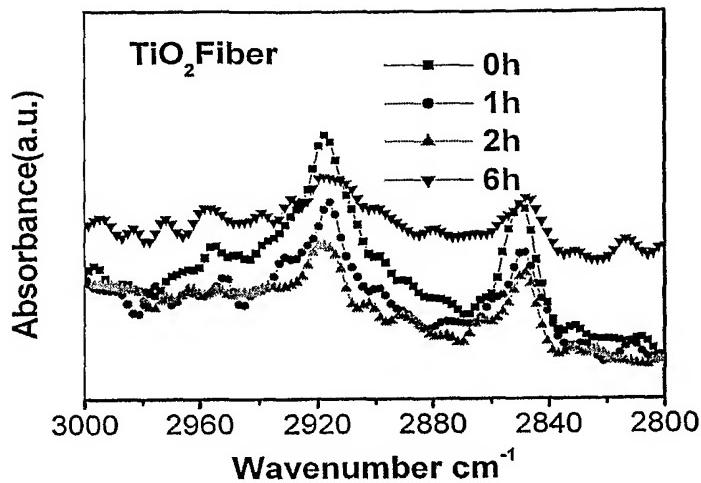


Figure 2A

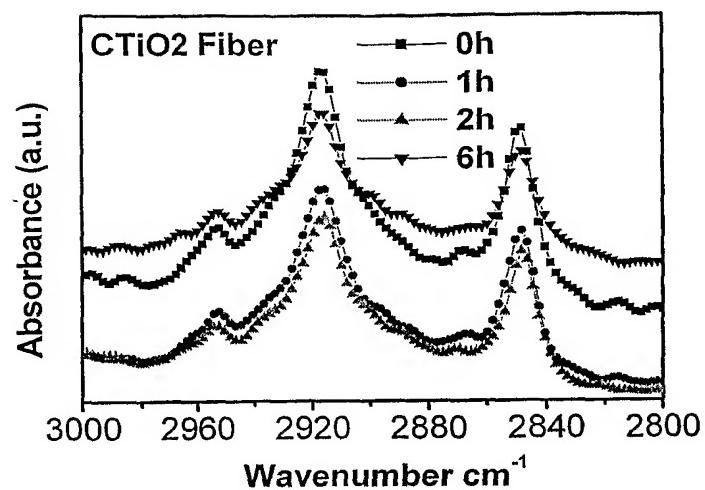


Figure 2B

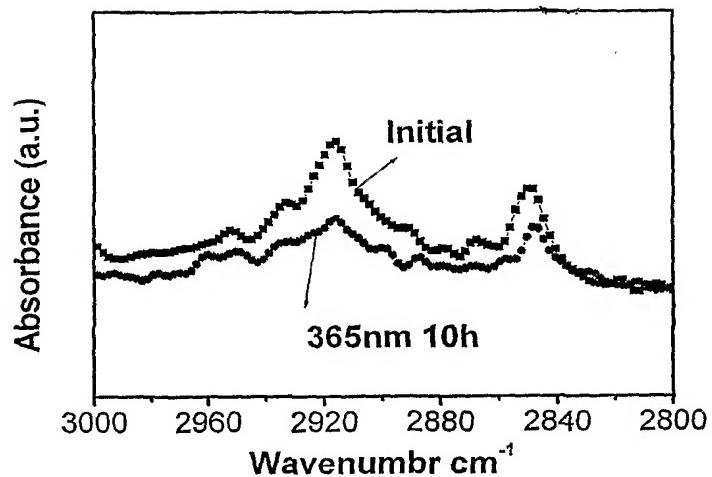


Figure 3A

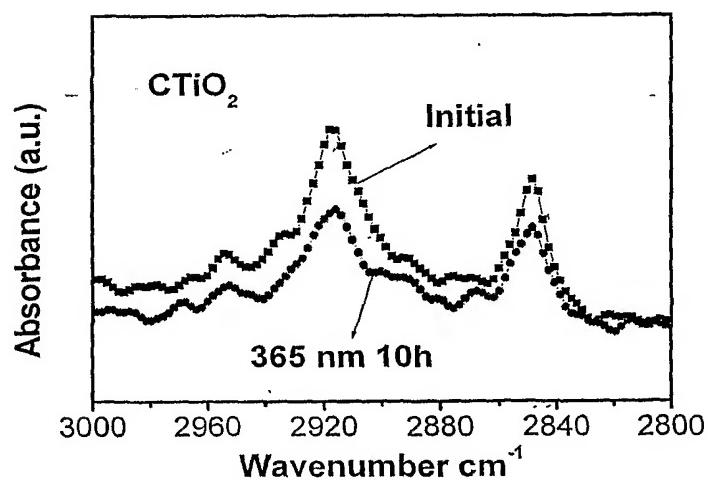


Figure 3B

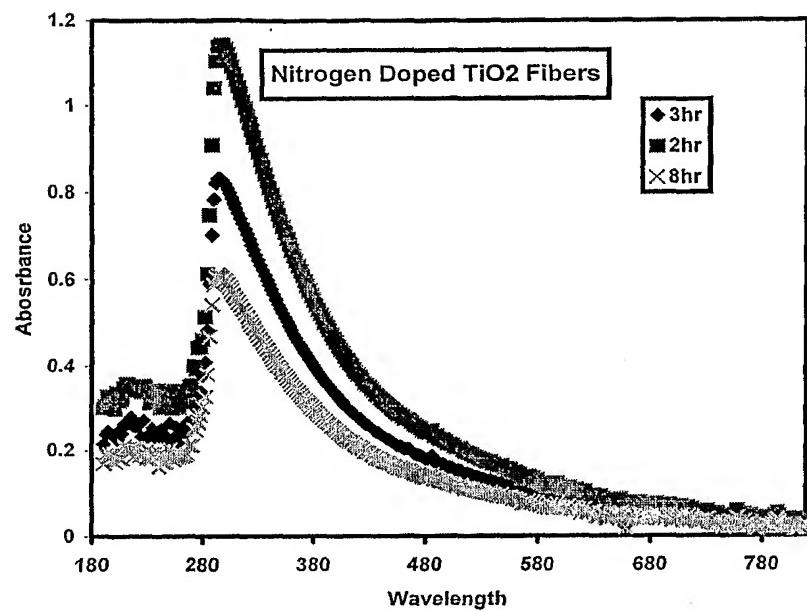
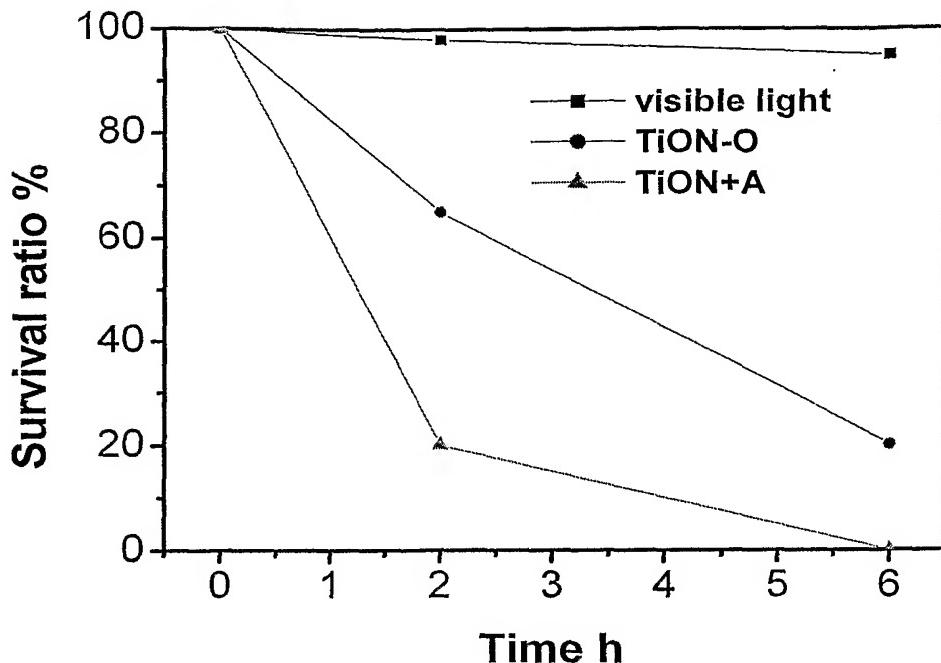
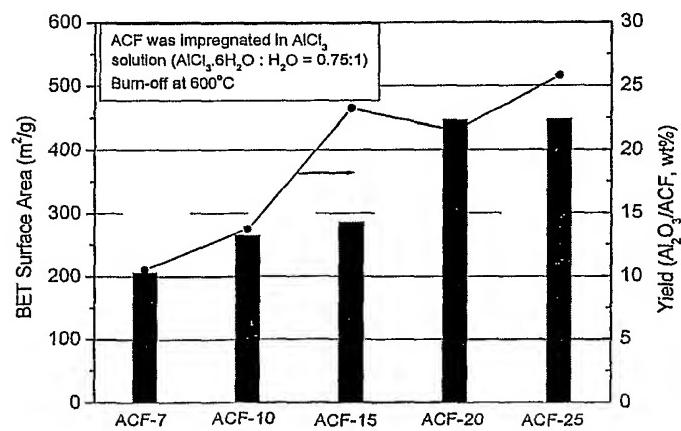
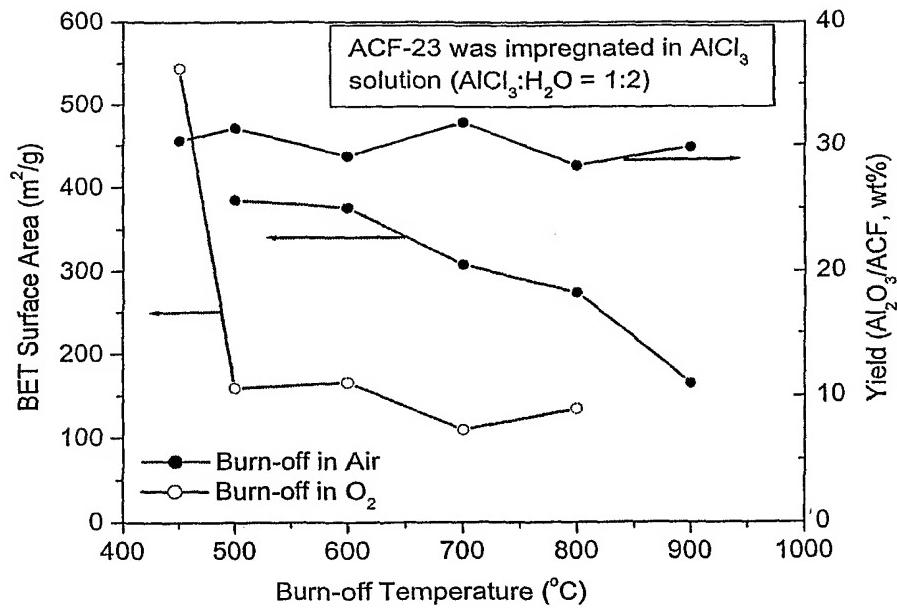
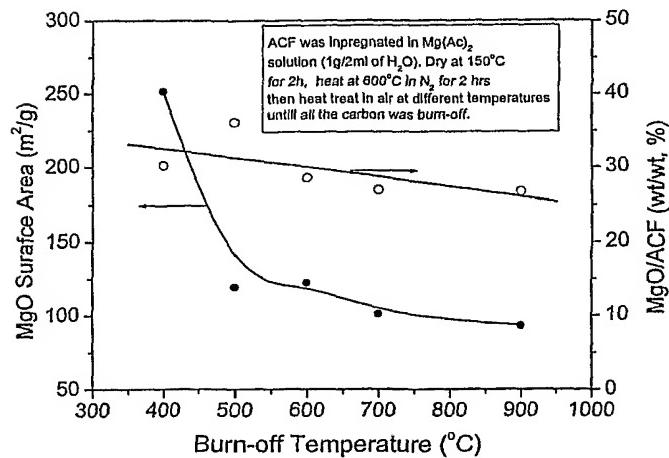


Figure 4

**Figure 5****Figure 6**

**Figure 7****Figure 8**

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2005/008008

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C03C25/10 C03C25/42

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 827 856 A1 (SAINT GOBAIN QUARTZ) 31 January 2003 (2003-01-31) abstract page 1, line 18 - line 23 example 4; table 5 -----	11-23, 26-30
A	GB 2 155 458 A (* FIBER MATERIALS INC) 25 September 1985 (1985-09-25) abstract -----	1-30

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

13 July 2005

Date of mailing of the international search report

22/07/2005

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US2005/008008

Patent document cited in search report	Publication date		Patent family member(s)	Publication date
FR 2827856	A1	31-01-2003	CN 1558878 A EP 1409428 A1 WO 03010106 A1 JP 2004536014 T US 2004197552 A1	29-12-2004 21-04-2004 06-02-2003 02-12-2004 07-10-2004
GB 2155458	A	25-09-1985	US 4543121 A DE 3507588 A1 FR 2568898 A1 JP 60209017 A BE 901918 A1 CA 1236307 A1 DE 3506564 A1 GB 2155457 A	24-09-1985 05-09-1985 14-02-1986 21-10-1985 01-07-1985 10-05-1988 03-10-1985 25-09-1985